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Crystallization under elongation of a polypropylene

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Abstract

A new method is able to study by optical microscopy the crystallization (nucleation and growth) under elongation and their enhancement from static condition. The nucleation and growth rate are analyzed as a function of the local strain-rate measured in-situ.

1. Introduction

The crystallization is a key point for polymer processing, structure development and properties. The crystallization kinetics depends on polymer, crystallization temperature, flow and pressure. The kinetics of most polymers is usually well known under static condition, for the main ones, under shear [1, 2] and under pressure. Very few data are available for crystallization after or under elongation but it is known as very efficient on the kinetics. A new device is able to apply an isothermal experiment after a quick cooling and to observe directly the morphologies.

2. Experimental device and procedure

The basic machine is a Minimat tensile machine (PolymerLab) with a 20 N load sensor. A new oven was redesigned in order to heat and cool homogeneously the sample. It consists in an oven isolated by a PTFE with two double-layer transparent windows, up and down. The sample is locally heated by a symmetric flux of preheated nitrogen allowing a quick cooling ($dT/dt \sim 20^\circ\text{C}/\text{min}$) and a good isothermal control ($\Delta T_{\text{max}} < 0.5^\circ\text{C}$). Three Pt100 thermal sensors are implanted in the machine for the thermal regulation: one near the heater, two at 1 mm of the sample. A small sample (free-length = 3 mm, width = 8 mm, thickness = 0.5 mm) of an isotactic polypropylene Atofina 3030BN1 ($M_n = 52\,000$, $M_w = 340\,000$) is fixed between jaws to be observed under polarized light and recorded with video cameras. The sample is heated to and cooled down from 210°C at a rate $dT/dt \sim 20^\circ\text{C}/\text{min}$ to the crystallization temperature and the stretched a constant speed (20 mm/min) with recording. The step at 210°C is critical, above the equilibrium melting temperature ($T_f^\circ > 208^\circ\text{C}$) [3], and there is no specific drop of the sample thanks to the small length and its large width but with a possible shrink.

3. Experimental results

Crystallizations under static condition, without stretching are necessary for the thermal calibration by measurement of the spherulite growth-rate as a tracer for temperature. The α -phase spherulites are randomly distributed and the growth rate is constant in the middle of the sample ($G_{\text{static}} = 0.25\ \mu\text{m}/\text{s}$) which are significant to a very low thermal gradient and stable temperature.

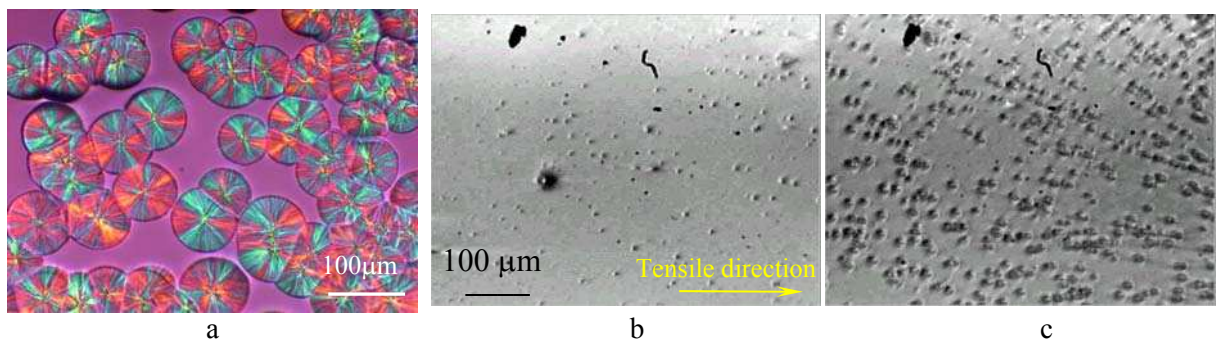


Figure 1: $T_c = 127^\circ\text{C}$; a, static crystallization; b and c during elongation; b, 14s ; c, 35s

At the beginning of elongation experiment the spherulites are randomly distributed (Fig. 1b). Their number progressively increases and they are progressively aligned along the tensile direction (Fig. 1c). The crystalline growth seems to be mainly in the form of α -phase spherulites (circular shape). At the end of experiments voids appear and develop in the film along the stretching direction leading to fibrils where the crystalline morphologies ended to crystallize.

3.1 Nucleation under elongation

From all the pictures (selection in Figs. 1b-c) it is possible to count the number of spherulites, i.e. the activated nuclei, as a function of time in static and under elongation and to measure the growth rate of different spherulites (Fig. 2).

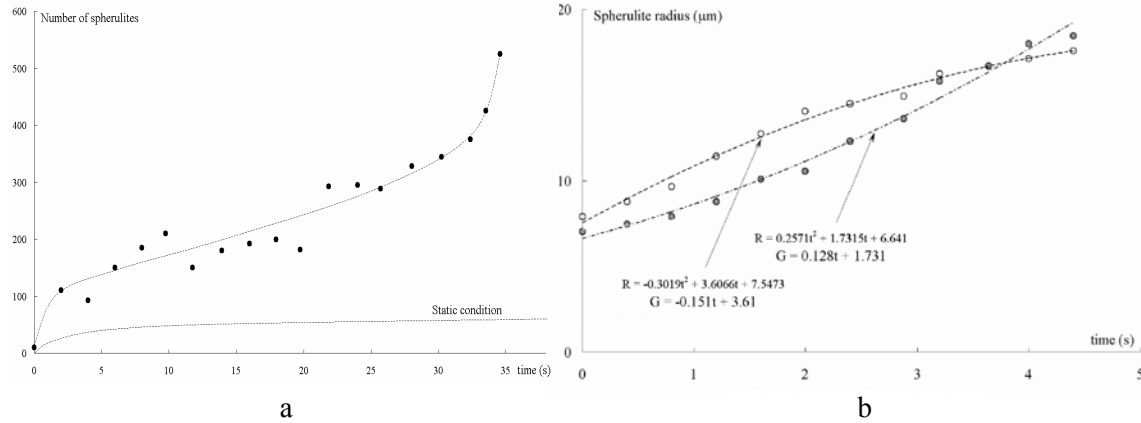


Figure 2 □ Nucleation and growth-rate under static and elongation ($T_c = 127^\circ\text{C}$)

The deformation is not homogeneous in the sample and is tracked locally by measurement of spacing change between two spherulites in the axial direction. The local strain-rate increases from 0.17 s^{-1} to 0.24 s^{-1} and is significantly higher than the nominal value 0.11 s^{-1} .

In static condition, the number of spherulites reaches an asymptote ($N_{\text{max}} \sim 60$ nuclei). Under elongation their number progressively increases to about ten times the value observed in static condition (Fig. 2a). The aligned spherulites are formed at the end of experiment (Fig. 1c).

The crystalline growth in that experiment is isotropic, leading to spherulites. The isotropy of the crystalline growth seems to be connected to the random nucleation. We have observed a similar behavior during crystallization under shear [1]. The growth rate analysis is simplified, only a radial value is needed. It is possible to compare the growth rate of the same crystalline phase (α -phase). We know now the local growth rate and local mechanical history (strain, strain-rate) and the kinetic analysis can be done (Fig. 2b).

The mean growth-rate of spherulites $2\text{ }\mu\text{m.s}^{-1} < G_{\text{elongation}} < 3\text{ }\mu\text{m.s}^{-1}$ is about ten times the growth-rate in static condition $G_{\text{static}} = 0.25\text{ }\mu\text{m.s}^{-1}$. A growth-rate increase was observed previously under shear for different molecular weights [2] but for a high shear rate $\dot{\gamma} \sim 40\text{ s}^{-1}$ while only $\dot{\alpha} \sim 0.2\text{ s}^{-1}$ is sufficient to obtain the same effect. We can conclude that elongation is much more efficient than shear to increase the crystalline growth-rate. The growth-rate increase is the main factor acting on the overall kinetics

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